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The Symmetric Group in Quantum Chemistry

Ruben Pauncz



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THE SYMMETRIC GROUP IN QUANTUM CHEMISTRY

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Preface

In the early applications of quantum mechanics (1926-1930) to the problem of the structure of the atoms and molecules an extensive use was made of group theoretical methods. The main tool was the symmetric group and its representations. In this treatment one had to consider the symmetry properties of the spinfunctions and of the spatial functions and one had to take into account the fact that in order to have the proper overall symmetry of the many electron wavefunctions the allowed representations of the spatial functions should be the conjugate representations generated by the spin functions. This treatment originated with the papers of Heisenberg, Heitler, Weyl, Hund and Wigner. It necessitated a good knowledge of the theory of the symmetric group and its representations. At that time group theory was not a common knowledge of physicists and chemists and this fact made the application of the theory quite cumbersome.

The situation changed quite dramatically with the appearance of Slater's paper in 1931. He introduced the determinantal formulation of the wavefunction which contains both spin and spatial variables. The determinantal form assures that the total wavefunction satisfies the antisymmetry principle, and one has not to worry about the representations generated by the spin functions and by the spatial functions. Slater and Condon showed that the matrix elements of the Hamiltonian could be calculated quite easily between two determinantal wavefunctions if they are built up from a set of orthogonal functions. The Slater-Condon rules can also be generalized to the case when the determinants contain nonorthogonal functions (Löwdin). This approach became very popular and Slater proudly announced that "he has eradicated the Gruppenpest." The determinantal method became the basis of several treatments. Optimizing the orbitals in the determinant for the total energy lead to the Hartree-Fock (self-consistent-field) treatment which provided an excellent starting point for most atomic and molecular

calculations. The linear combinations of determinants lead to the configuration interaction treatment which allowed a considerable improvement over the single-determinantal treatment.

The determinantal treatment is well adapted to the treatment of the structure of atoms and molecules. It still has some drawbacks for the interpretation of the wavefunction. Because it contains both spatial and spin variables it leads very easily to some misconceptions about the role of spin in the energetics. In most molecular and atomic calculations one uses a Hamiltonian which does not include the spin variables (spin-free Hamiltonian), but the determinantal approach obscures the fact that the expectation value of the Hamiltonian depends only on the spatial functions.

In recent years there was a revival in the interest of treatment which shows more clearly this fact. The so called spin-free quantum chemistry has now a quite wide literature. The aim of the book is to present this approach in a self-contained fashion. So we shall start first with the conventional approach (Slater determinants) and review the spin-free Hamiltonian used in most molecular and atomic calculations and the basic rules for the calculation of the matrix elements between determinantal wavefunctions which involve both spatial and spin variables. Then we shall present the theory of the symmetric group; in this part we shall emphasize those notions which will be necessary for our treatment. A separate chapter will deal with the representations of the symmetric group generated by the spinfunctions and another chapter deals with the proper combination of spatial and spinfunctions. The heart of the book is in the chapter dealing with spin-free quantum chemistry. It will show the interpretation value of this treatment and also show that computationally this approach is not inferior to the conventional treatment. Another approach which is also based on the spin-free treatment is the unitary group approach; we shall give a short summary of this treatment. The next chapter will show how one can organize very effectively the calculations for the many-electron problem using the symmetric group approach. An alternative treatment which also uses the representations of the symmetric group is the so called spin-coupled wavefunctions and the spin-coupled valence bond method is presented in the last chapter. A fairly extensive bibliography concludes the book.

The book is an introduction to these subjects, there are many simple examples worked out in detail. It can be used either as a text book for a one semester graduate course or for independent study.

The author would like to express his thanks to Prof. D.J. Klein, for asking him to write this monograph, to Prof. F.A. Matsen who introduced him to this subject and for his wonderful contributions to spin-free quantum chemistry. The author is grateful to Prof. P.O. Löwdin and to other members of the Uppsala Quantum Chemistry Group for organizing the numerous Summer Institutes in Quantum Chemistry and Solid State Physics where the author lectured on some of the subjects presented in this book.

The author is grateful to Prof. J. Katriel for his important contributions to the representation theory of the symmetric group and for letting the author participate in some of these papers. Sincere thanks are due to Prof. N. Moiseyev for many discussions and for his research group's interest in the subject. Thanks are due to Prof. S. Rettrup for his hospitality during the visit to Copenhagen, for reading part of the manuscript and for helpful remarks. The author is grateful to Prof. J. Gerratt and to Prof. Jiabo Li for sending some unpublished results. The author is grateful to Prof. E.A. Halevi for introducing him to the use of LaTeX (the whole book including the tables were produced using this language). The author is grateful to the Editorial Staff at CRC Press and especially to Ms. Gail Renard for their expert handling of the manuscript. Last but not least I would like to express my gratitude to Kathy and my family for their moral support while working for the last two years on the book.

Ruben Pauncz
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Contents

1	The quantum mechanical background	1
1.1	Introduction	1
1.2	Spin-free Hamiltonian	1
1.3	The antisymmetry principle	3
1.4	Atomic and molecular orbitals	4
1.5	Slater determinant	5
1.6	The self-consistent-field method	7
1.7	Configuration interaction method	8
1.8	Slater-Condon rules	10
1.9	Löwdin rules	12
2	The symmetric group	19
2.1	Introduction	19
2.2	Permutations	19
2.3	The symmetric group	20
2.4	Cyclic permutation	20
2.5	Classes of the symmetric group	23
2.6	Subgroups of the symmetric group	25
2.7	Double cosets	27
3	Representation of S_N	31
3.1	Reps of the symmetric group	31
3.2	Young tableaux	32
3.3	Young's orthogonal representation	36
3.4	The branching law of the symmetric group	38
3.5	The conjugate representation	40
3.6	The coset representation	42
3.7	Decomposition of the coset representation	46
3.8	Characters of the symmetric group	48
3.9	Calculation of the characters	58
3.10	The subgroup $S_2 \otimes S_2 \dots \otimes S_2$	62
3.11	Appendix 1	63

4	The symmetric group algebra	67
4.1	Algebraic notions	67
4.2	Class operators	69
4.3	Matric basis of the group algebra	72
4.4	Matric basis for the centrum of the algebra	75
4.5	The Young operator basis ³	79
5	Spin eigenfunctions	95
5.1	Introduction	95
5.2	Construction of spin eigenfunctions	95
5.3	The genealogical construction	96
5.4	The branching diagram	98
5.5	Reps of the S_N generated by the spinfn's	102
5.6	Yamanouchi-Kotani method for the reps	105
5.7	Branching diagram fn's and Young tableaux	108
5.8	Serber spin functions	112
5.9	Projected spin eigenfunctions	115
5.10	Spin-paired spin eigenfunctions	123
5.10.1	Correspondence between spin-paired functions and Young tableaux.	131
6	Spatial functions	135
6.1	Antisymmetric wavefunction	135
6.2	Decomposition of the wavefunction	137
6.3	Reps of S_N by the spatial functions	138
6.4	Branching diagram functions	139
6.5	Serber wavefunction	141
6.5.1	Normalization integral	143
6.5.2	The lineup permutation	143
6.5.3	The wavefunctions form an orthonormal set	144
6.5.4	The form of the Hamiltonian	145
6.5.5	Reduction of the sum over the permutations	145
6.5.6	Reduction of the sum over electron pairs	147
6.5.7	Matrix elements of the Hamiltonian for special cases	148
6.6	Projected wavefunction	149
6.7	Valence bond wavefunction	152
7	Spin free quantum chemistry	157
7.1	Introduction	157
7.2	Orbital product functions	157
7.3	Invariance group of the primitive ket	158
7.4	Spin free exclusion principle	161
7.5	Structure projections	163
7.5.1	The pair diagram	163

7.5.2	The pair operators	165
7.5.3	Spin free pair functions	167
7.5.4	Pair projections in the function space	168
7.5.5	Spin free exclusion principle for structure projections	169
7.6	Spin free counterpart of $\mathcal{A}\Phi V_k^S$	170
7.7	Spin free counterpart of the projected fn	175
7.8	Gallup's tableau operators	180
7.9	Calculation of the Pauling numbers	183
7.10	Li's algorithm	186
8	Unitary group approach	195
8.1	Introduction	195
8.2	Basic notions	195
8.3	Tensor space	201
8.4	Model Hamiltonian	203
8.5	Reps of the unitary group	206
8.6	The branching law of the unitary group	209
8.7	Representation matrices of the generators	210
8.8	Weyl tableaux	217
8.9	Electronic Gel'fand state	219
8.10	Paldus arrays	221
8.11	Graphical unitary group approach	233
8.12	Direct configuration interaction method	248
9	Symmetric group approach in CI	253
9.1	Introduction	253
9.2	Representation matrices	254
9.3	Sarma and Rettrup algorithm	258
9.4	Duch and Karwowski algorithm	267
9.5	Symmetric group graphical approach	274
10	Spin-coupled functions	281
10.1	Introduction	281
10.2	Historical development	282
10.3	Spin-coupled wavefunctions	286
10.4	SCVB functions	289
10.5	Core-valence s-c wavefunction	290
	Bibliography	295
	Index	321



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1

The quantum mechanical background

1.1 Introduction

In the present chapter we shall review very briefly the conventional determinantal treatment. We start with the spin-free Hamiltonian used in a large number of atomic and molecular calculations. We introduce the antisymmetry principle and show the construction of antisymmetric wavefunctions using the product of spatial and spinfunctions. A frequently used approximation is the representation of the wavefunction by a single determinant in which every orbital occurs twice (for an even number of electrons). The optimization of the orbitals leads to the Hartree-Fock (self-consistent-field) method. The matrix elements of the Hamiltonian between determinantal functions are presented both for the case of orthogonal and non-orthogonal orbitals. We review the basic principles of the configuration interaction method.

1.2 Spin-free Hamiltonian

In most atomic and molecular calculation one uses the following Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^N \left[-\frac{1}{2} \nabla_i^2 - \sum_{\alpha=1}^{\nu} \frac{Z_{\alpha}}{r_{i\alpha}} \right] + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{\alpha=1}^{\nu} \sum_{\beta>\alpha}^{\nu} \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}} \quad (1.1)$$

In Eq.(1.1) the first term is the operator corresponding to the sum of the kinetic energy of the N electrons, the second term corresponds to the sum of the attractions between the electrons and the nuclei, the third term corresponds to the interelectronic repulsions and the final term describes

mass	m_e	mass of the electron
charge	e	-charge of the electron
angular momentum	$\frac{h}{2\pi}$	$\equiv \hbar$
length	a_0	$\frac{h^2}{4\pi^2 m_e e^2} = \text{bohr}$
energy	E_H	$\frac{e^2}{a_0} = \text{hartree}$

TABLE 1.1
Atomic units

the nuclear-nuclear repulsions. $r_{i\alpha}$ is the distance between electron i and the nucleus α , $R_{\alpha\beta}$ is the distance between nuclei α and β with the charges Z_α and Z_β , respectively, ν is the number of nuclei. The operator ∇^2 is defined as follows:

$$\nabla^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

Here x_i, y_i, z_i are the coordinates of the i 'th electron. All the quantities are expressed in atomic units. Table 1.1 contains the definitions of the atomic units which will be used in the following:

The use of the Hamiltonian given in Eq.(1.1) involves several approximations:

(a) The Born-Oppenheimer approximation.¹ One considers the nuclei being in a fixed position and one calculates the electronic wavefunction. One repeats the calculation for various positions of the nuclei.

(b) One neglects various small terms in the Hamiltonian which correspond to spin-orbit interaction, spin-spin interaction, orbit-orbit interaction, and other relativistic effects.

The reason for neglecting these terms is that their effect is relatively small and if one is not interested in finer effects they can be neglected. For a review of weak interactions and molecular fine structure see the papers of Karplus² and Langhoff and Kern.³ Matsen⁴ calls the use of this Hamiltonian : *a coarse structure chemistry*. This Hamiltonian does not explicitly include the spin variables, it is a spin-free Hamiltonian.

1.3 The antisymmetry principle

Before formulating the antisymmetry principle we would like to look at the way the principle was discovered. The first step was the *exclusion principle* found by Pauli⁵ in 1925. This was before the new quantum mechanics was discovered, so Pauli's paper is still based on the concept of electronic orbits, as defined in the old quantum theory of Bohr. It tells that in the atom there are no two electrons for which the four quantum numbers are the same. The physical meaning of the fourth quantum number was not clear at that time, since spin was not yet discovered though Pauli⁶ already in the fall of 1924 used the notion of the two-valuedness of the quantum theoretic properties of the electron which later turned out to be connected with the existence of the spin. The spin hypothesis was introduced the same year by Uhlenbeck and Goudsmit^{7,8}. An excellent survey about the exclusion principle and spin is found in van der Waerden's paper.⁹

The next step was made by Heisenberg^{10,11} in 1926 shortly after the discovery of quantum mechanics. He published two papers in which he considered the quantum mechanics of a system containing two identical particles and showed that the states divided into completely symmetric and completely antisymmetric states. No transition from one type to the other could be caused by any disturbance which maintained the identity of the particles. He showed that the antisymmetric states corresponded to those permitted by the exclusion principle, and used the results for a detailed discussion of the ortho and para states of the helium atom.

In the same year appeared the paper of Dirac¹² dealing with systems of identical particles. Here Dirac starts from the requirement that the theory should not make statements about unobservable quantities, and therefore for two identical particles which may be in the quantum states m and n , resp. the state n , m should not be counted separately from m , n . He also remarks that the antisymmetric states are those satisfying the exclusion principle and they are appropriate for electrons in atoms, whereas the symmetric states are applicable to photons.

After these historical remarks let us formulate the antisymmetry principle. For sake of simplicity consider a system of two electrons. The probability of finding electron 1 in the neighborhood of the space point with the coordinates x_1, y_1, z_1 and with the spin coordinate ζ_1 , and electron 2 in the neighborhood of the space point x_2, y_2, z_2 and spin coordinate ζ_2 is given by the expression:

$$\Psi^*(x_1, y_1, z_1, \zeta_1; x_2, y_2, z_2, \zeta_2) \Psi(x_1, y_1, z_1, \zeta_1; x_2, y_2, z_2, \zeta_2) dv_1 dv_2 d\tau_1 d\tau_2$$

As the electrons are identical, one cannot distinguish between them and the same probability should be assigned to the event in which the two

electrons are interchanged. For the wavefunction itself this leaves two possibilities: either it will remain the same (symmetric) or it will change sign (antisymmetric). Pauli¹³ has shown in general that particles with half integer spins (like the electron) correspond to the second possibility. The wavefunction should change sign by the interchange of two electrons. In the next chapter on the symmetric group we shall see that an arbitrary permutation of the coordinates can be expressed as a product of transpositions, so the final form of the antisymmetry principle reads as follows:

$$P\Psi(1, \dots, N) = (-1)^p \Psi(1, \dots, N) \quad (1.2)$$

Here p is the number of transpositions into which the permutation could be decomposed (the parity of the permutation).

Electrons are *fermions*, they obey the Fermi-Dirac statistics and their wavefunction has to satisfy the conditions posed by the antisymmetry principle. The wavefunction vanishes if two electrons have the same spatial and spin coordinates. In Chapter 6 we shall discuss how one can construct general wavefunctions which satisfy the antisymmetry principle. In the next section we shall discuss the approximation of the wavefunction by products of one- electron functions (called *orbitals*) and then the determinantal form of this kind of wavefunction.

1.4 Atomic and molecular orbitals

The Hamiltonian could be replaced by an approximate one which is the sum of one-electron terms. In the crudest way one can get this type of Hamiltonian if one omits the two-electron terms (electron-electron repulsion). In a more sophisticated way one can replace the sum of the electron-electron repulsion by a sum of one-electron terms in which each term represents the average potential felt by a single electron in the field of the other electrons. We shall discuss this approach in the next section.

When we use the approximate Hamiltonian \mathcal{H}' the eigenfunctions can be written as a product of one-electron functions:

$$\mathcal{H}' = \sum_{i=1}^N h'(i) \quad \Psi = \phi_{i_1}(1) \dots \phi_{i_N}(N)$$

$$h'(i)\phi_j = e_j\phi_j \quad \mathcal{H}'\Psi = E\Psi \quad E = \sum_{j=1}^N e_j$$

These one-electron functions are called *orbitals*. Following Matsen we shall call them *freeon orbitals*, they are solutions of one-electron Hamiltonians. These orbitals have to be combined with *spin orbitals*, in Pauli's treatment¹⁴ there are two basis functions α and β which are eigenfunctions of the S_z operator with the eigenvalues $\frac{1}{2}$ and $-\frac{1}{2}$ respectively. In the final wavefunction we have the product of freeon and spin functions, the product will be called a *fermion orbital*. The freeon orbitals are called *atomic* or *molecular orbitals* if they are obtained from the solution of the approximate atomic or molecular Hamiltonian. They can be chosen as an orthonormal set.

1.5 Slater determinant

Slater¹⁵ proposed a very simple procedure for the construction of antisymmetric wavefunction from the products of fermion orbitals. Let us form a determinant in which the orbitals $\phi_{i_1} \dots \phi_{i_N}$ appear in the N columns of the determinant and the different rows correspond to the variables from 1 to N :

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{i_1}(1) & \dots & \phi_{i_N}(1) \\ \vdots & \dots & \vdots \\ \phi_{i_1}(i) & \dots & \phi_{i_N}(i) \\ \vdots & \dots & \vdots \\ \phi_{i_1}(N) & \dots & \phi_{i_N}(N) \end{vmatrix}$$

The determinant changes sign when we interchange two rows (interchange of two electrons as the rows refer to the electronic variables). The determinant vanishes if two columns are the same, i.e. the product cannot contain the same fermion orbital more than once, or the freeon orbital may occur at most twice once with α and the second time with β spinfunction. This is a simple representation of the Pauli exclusion principle.

Using the definition of the determinant given by Cauchy we can write the above expression in the following form:

$$\Psi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_{i_1}(1) \dots \phi_{i_N}(N)$$

Here P means a permutation of the electronic coordinates, we shall discuss their properties in the next chapter. Let us define the following operator:

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \quad (1.3)$$

We shall call this operator the *antisymmetrizer*, it produces an antisymmetric wavefunction when applied to a simple product function. In Chapter 4 Section 1 we shall prove that the operator is hermitean, it commutes with the Hamiltonian and its square is proportional to itself:

$$\mathcal{A}^2 = \sqrt{N!} \mathcal{A} = \sum_P (-1)^P P \quad (1.4)$$

A fermion orbital ϕ_i can be written as a product of spatial (freeon) ψ_i and a spin orbital σ_i , the latter can be either an α or a β spinfuction corresponding to the s_z eigenvalue $\frac{1}{2}$ or $-\frac{1}{2}$, respectively.

The antisymmetrizer commutes with the operator $S_z = \sum_{i=1}^N s_z(i)$ so each Slater determinant is an eigenfunction of S_z with the eigenvalue: $M = \frac{1}{2}(\mu - \nu)$, where μ and ν are the number of α and β spinfuctions, respectively. A single Slater determinant is in general not an eigenfunction of the resultant S^2 operator.

Closed shell function. Let us assume that we have an even number of electrons: $N=2n$. Let us form a Slater determinant in which each of the spatial orbitals $\psi_i, i = 1, \dots, n$ occurs twice, once with an α and once with a β spinfuction:

$$\Psi = \mathcal{A}\psi_1(1) \dots \psi_n(n)\psi_1(n+1) \dots \psi_n(2n)\alpha(1) \dots \alpha(n)\beta(n+1) \dots \beta(2n)$$

This wavefunction is an eigenfunction of S_z with the eigenvalue 0. One can also show that this single determinant is also an eigenfunction of S^2 with the eigenvalue 0, it corresponds to a singlet state.

Slater's proposal was immediately accepted and it became the cornerstone of the further development of quantum chemistry. It was much simpler than the use of group theoretical methods for the construction of the total wavefunction. Slater could tell that he eradicated "the group pest" from quantum mechanics. It served as a starting point both for the self-consistent-field method and for the configuration interaction treatment. We shall discuss these methods in the next sections. The great advantage of this method was that it was easy to calculate the matrix elements of the Hamiltonian between two determinantal wavefunctions built up from orthogonal orbitals. We shall present the Slater-Condon rules for the calculation of the matrix elements in Sec.1.8.

1.6 The self-consistent-field method

Let us choose as a starting point a single Slater determinant with doubly occupied orbitals (closed shell function) defined in the previous section. One can ask the question what are the best freeon orbitals ψ_1, \dots, ψ_n . As a possible criterion for the choice of the best orbitals one can use the variation principle and ask for those orbitals which minimize the total energy:

$$E = \langle \Psi | \mathcal{H} | \Psi \rangle$$

Hartree¹⁶ has derived the equation for the determination of the best orbitals by using a simple product function and Fock¹⁷ obtained the equation for the antisymmetrized product function. The best orbitals are the solutions of the following equations:

$$F\psi_i = \epsilon_i\psi_i \quad (1.5)$$

The Fock operator F appearing in Eq.(1.5) is defined as follows:

$$F = h + \sum_{i=1}^n (2J_i - K_i) \quad (1.6)$$

Here h is the one-electron operator, it is the sum of the kinetic energy operator and the operator corresponding to the attraction of the electron to the nuclei. In the above equation appear two operators J_i and K_i , these are defined in terms of the solutions ψ :

$$J_j(1)\psi_i(1) = \left(\int \frac{\psi_j^*(2)\psi_j(2)}{r_{12}} dv_2 \right) \psi_i(1) \quad (1.7)$$

$$K_j(1)\psi_i(1) = \left(\int \frac{\psi_j^*(2)\psi_i(2)}{r_{12}} dv_2 \right) \psi_j(1) \quad (1.8)$$

The physical meaning of the first operator called the *Coulomb operator* is quite simple: it represent the potential due to an electron which is in orbital ψ_j . The meaning of the second operator called the *exchange operator* is more complicated. It appears because of the antisymmetry principle (this operator is missing in the simple Hartree method), when acting on orbital ψ_i it replaces it by the orbital ψ_j and multiplies it by the integral which involves the product of orbitals ψ_i and ψ_j . What is important to observe is that the operators depend on the solutions, so the equations can be solved only in steps: One starts with a given set of orbitals, one calculates the Coulomb and exchange operators, and one solves the equations. The

solutions are used in the next step to calculate the operators. One continues this procedure until one arrives at self consistency i.e. the solutions provide operators and the next solution do not differ from those which have been used in constructing the operators.

The self-consistent-field (Hartree-Fock) method gained wide acceptance when Roothaan¹⁸ formulated it in the matrix form. Let us assume that the orbitals ψ are given as linear combinations of basic orbitals χ 's:

$$\psi = \sum_{\mu=1}^M \chi_{\mu} c_{\mu i}$$

Here M is the dimension of the basis set, i.e. the number of basic orbitals. The eigenvalue problem is now a matrix eigenvalue equation:

$$\sum_{\nu=1}^M F_{\mu\nu} c_{\nu i} = \epsilon_i \sum_{\nu=1}^M S_{\mu\nu} c_{\nu i} \quad (1.9)$$

The matrix elements of the Fock operator are given as follows:

$$F_{\mu\nu} = \langle \mu | h | \nu \rangle + \sum_{\rho} \sum_{\sigma} P_{\rho\sigma} [2(\mu\nu | \rho\sigma) - (\mu\sigma | \rho\nu)] \quad (1.10)$$

In Eq. (1.10) appear elements of the charge and bond order matrix:

$$P_{\mu\nu} = 2 \sum_{i=1}^n c_{\mu i}^* c_{\nu i}$$

and some two electron integrals involving the basis orbitals. In the latter we have used the following notation:

$$(\mu\nu | \rho\sigma) = \int \int \frac{\chi_{\mu}^*(1) \chi_{\nu}(1) \chi_{\rho}^*(2) \chi_{\sigma}(2)}{r_{12}} dv_1 dv_2 \quad (1.11)$$

Again one can observe that Eq.(1.9) is not a proper eigenvalue equation as the matrix elements of Fock operator depend on the elements of the charge and bond-order matrix which themselves contain the coefficients of the molecular orbitals to be determined.

1.7 Configuration interaction method

The self-consistent-field method provides an excellent first approximation. It can predict bond lengths and charge densities with great accuracy. The

total energy is predicted usually with an accuracy of 99.5%. For most chemical purposes one does not need the total energy but rather energy differences as excitation energies, transition state energies and so on. The small error in the total energy could be a very large error in predicting energy differences. It is necessary therefore to go beyond the Hartree-Fock approximation. Löwdin¹⁹ has defined the *correlation energy* as the energy difference between the Hartree-Fock solution and the full non-relativistic Hamiltonian. There are several methods to deal with the correlation problem, the most systematic one is the *configuration interaction method*. Let us consider a wavefunction which is a linear combination of configuration wavefunctions.

$$\Psi = \sum_{i=1}^K \Psi_i c_i$$

The configuration wavefunctions can be written in the form:

$$\Psi = \mathcal{A} \psi_{i_1}(1) \dots \psi_{i_N}(N) X(1, \dots, N)$$

Here the freeon orbitals $\psi_{i_1} \dots \psi_{i_N}$ are chosen among the set of orbitals $\psi_1 \dots \psi_M$ and $X(1, \dots, N)$ is a spin eigenfunction of the operator S^2 :

$$S^2 X(1, \dots, N) = S(S+1) X(1, \dots, N)$$

About the construction of spin eigenfunctions we shall speak in detail in Chapter 3. Each eigenfunction is a linear combination of a number of *primitive spinfunctions* which themselves are products of α and β spinfunctions. From this follows that a configuration function is a linear combination of several Slater determinants. The linear coefficients are determined by the construction of the spin eigenfunction.

The total wavefunction is a linear combination of configuration functions. Here the linear coefficients can be determined from the variational principle (minimization of the total energy), the coefficients are solutions of the secular equations:

$$\sum_j (H_{ij} - E S_{ij}) c_j = 0$$

In the equation we have matrix elements of the Hamiltonian and of the identity operator between configuration functions:

$$H_{ij} = \langle \Psi_i | \mathcal{H} | \Psi_j \rangle$$

$$S_{ij} = \langle \Psi_i | \Psi_j \rangle$$

For the calculation of the matrix elements we need to know the matrix elements of the Hamiltonian between the determinantal functions. In the next sections we shall present the Slater-Condon rules for the case when the orbitals form an orthonormal set and the Löwdin²⁰ rules which are valid for the more general case (the orbitals are not necessarily orthogonal).

1.8 Slater-Condon rules

Let us write the Hamiltonian in the following form:

$$\mathcal{H} = \sum_{i=1}^N h(i) + \sum_{i=1}^N \sum_{j>i}^N g(i, j) \quad (1.12)$$

h is the one-electron operator (the kinetic energy operator and the one corresponding to the attraction of the electron to the nuclei), $g(i, j)$ is the two-electron operator $g(i, j) = \frac{1}{r_{ij}}$, it corresponds to the electron-electron repulsion. Consider two determinantal functions:

$$\begin{aligned} \Psi_U &= \mathcal{A}u_1(1) \dots u_N = \mathcal{A}U \\ \Psi_V &= \mathcal{A}v_1(1) \dots v_N = \mathcal{A}V \end{aligned} \quad (1.13)$$

U and V are antisymmetrized products of fermion orbitals, which themselves are products of freeon and spin orbitals. The matrix element of the Hamiltonian between these determinantal function is given as follows:

$$\langle \Psi_U | \mathcal{H} | \Psi_V \rangle = \langle \mathcal{A}U | \mathcal{H} | \mathcal{A}V \rangle \quad (1.14)$$

We can use the turn-over rule: Remove the operator \mathcal{A} from the left side of the integral, and move it to the right by replacing it by its hermitean adjoint. The antisymmetrizer is hermitean, so its hermitean adjoint is equal to itself, and it commutes with the Hamiltonian:

$$\begin{aligned} \langle \Psi_U | \mathcal{H} | \Psi_V \rangle &= \langle U | \mathcal{H} | \mathcal{A}^2 V \rangle \\ &= \langle U | \mathcal{H} | \sum_P (-1)^P P V \rangle \end{aligned} \quad (1.15)$$

In the last step we used the fact that the square of the antisymmetrizer is proportional to itself (Chapter 6 Sec. 1), so instead of the $N!^2$ terms one has only $N!$ terms. The number of the terms which are different from zero is much smaller because of the orthogonality of the fermion orbitals. Only some of the permutations will yield nonvanishing results.

I) *One-electron operator.* Let us select only one term say $h(i)$ in the sum, and consider three different cases.

(a) The two determinants are the same: $V=U$. The only permutation which yields a nonvanishing result is the identity permutation, in all other cases we shall have an overlap integral between two orthogonal orbitals. The matrix element of the one electron operator between the determinant and itself is given as follows:

$$\langle U | \sum_{i=1}^N h(i) | U \rangle = \sum_{i=1}^N \langle u_i | h | u_i \rangle \quad (1.16)$$

(b) The two determinant differ in only one orbital. Let us use a rearrangement of the orbitals (this can change only the sign of the determinant) in such a way that orbitals $u_2 \dots u_N$ are the same in both determinants and only the first orbitals u_1 and v_1 are different. In this case only one term will contribute to the sum: these two orbitals have to appear together with the operator h under the integral sign, if they are outside, their orthogonality causes the vanishing of the term. In this case the matrix element reduces to only one term:

$$\langle U | \sum_{i=1}^N h(i) | U' \rangle = \langle u_1 | h | v_1 \rangle \quad (1.17)$$

(c) If the two determinants differ in more than one orbital than the matrix element is zero. (The one electron operator h can save only one pair from vanishing, the other has to appear outside the integral and its overlap integral is zero).

II) *The two-electron operator.*

Here we shall distinguish four cases, the first three are the same as earlier, the fourth one will be in which the two determinants differ in more than two orbitals.

(a) There are two permutations which can yield nonvanishing results: the identity permutation and the interchange between coordinates i and j .

$$\begin{aligned}
\langle U | \sum_{i=1}^{N-1} \sum_{j>i}^N g(i, j) | U \rangle = \\
\sum_{i=1}^{N-1} \sum_{j>i}^N \int \int u_i^*(1) u_j^*(2) \frac{1}{r_{12}} (u_i(1) u_j(2) - u_i(2) u_j(1)) d\tau_1 d\tau_2 \quad (1.18)
\end{aligned}$$

The integral is both over the spatial and spin variables.

(b) The two determinants differ in one pair of orbitals, these two orbitals have always to be under the integral sign together with the two electron operator, so we shall have only a single summation:

$$\langle U | G | U' \rangle = \sum_{i=1}^N \int \int u_1^*(1) u_i^*(2) \frac{1}{r_{12}} (v_1(1) u_i(2) - u_i(2) v_1(1)) d\tau_1 d\tau_2 \quad (1.19)$$

(c) In the third case there is only one contribution (consisting of two terms). Here we assume again a line up permutation, so the two determinants differ only in the first and the second orbitals. The final result reads:

$$\langle U | G | U'' \rangle = \int \int u_1^*(1) u_2^*(2) \frac{1}{r_{12}} (v_1(1) v_2(2) - v_1(2) v_2(1)) d\tau_1 d\tau_2 \quad (1.20)$$

(d) When the two determinants differ in more than two orbitals, the result is always zero, because the integral can “save” only two orbitals, and the third pair must appear outside the integral with a vanishing overlap integral.

1.9 Löwdin rules

The Slater-Condon rules for the calculation of the matrix elements of the Hamiltonian between determinantal functions are valid if the set of functions appearing in the determinants form an orthonormal set. There are several applications (mostly in the valence-bond method) where one uses basis functions (atomic orbitals) which are not orthogonal. Löwdin²⁰ derived the rules how to calculate the matrix elements of the Hamiltonian in this more general case.

Let us choose again the two determinantal functions Ψ_U and Ψ_V given in Eq. (1.13), but now the fermion orbitals appearing in the two determinants

do not have to belong to an orthonormal set. Let us denote the overlap integral between fermion orbital u_k and v_l in the following way:

$$\int u_k^*(1)v_l(1)d\tau_1 = d_{uv}(kl)$$

(a) *Matrix element of the identity operator.*

Let us calculate first the overlap integral between the two determinantal functions:

$$\langle \Psi_U | \Psi_V \rangle = \langle U | \sum_P (-1)^P P V \rangle = \langle U | \det(V) \rangle \quad (1.21)$$

$$= \sum_P (-1)^P \int u_1^*(1) \dots u_N^*(N) P v_1(1) \dots v_N(N) d\tau_1 \dots d\tau_N \quad (1.22)$$

Here the permutation P operates on the electronic coordinates. After the permutation has been performed we can rearrange the product in such a way that the coordinates appear in the natural order:

$$P v_1(1) \dots v_N(N) = v_{l_1}(1) \dots v_{l_N}(N) \quad (1.23)$$

The new indices of the orbitals v_{l_1}, \dots, v_{l_N} are obtained from the original indices by the inverse of the permutation P . Instead of summing over all the permutations we can as well sum over all the inverses, and this leads to the final result:

$$\langle \Psi_U | \Psi_V \rangle = \sum_P (-1)^P P d_{uv}(1l_1) \dots d_{uv}(Nl_N)$$

This expression is the determinant of the matrix whose elements are $d_{uv}(kl)$, we shall denote this matrix by D_{UV} . This matrix and its cofactors will play a central role in the evaluation of the matrix elements over the one and two-electron operators.

$$\langle \Psi_U | \Psi_V \rangle = \begin{vmatrix} d_{uv}(11) & \dots & d_{uv}(1N) \\ \vdots & \dots & \vdots \\ d_{uv}(i1) & \dots & d_{uv}(iN) \\ \vdots & \dots & \vdots \\ d_{uv}(N1) & \dots & d_{uv}(NN) \end{vmatrix} = \det D_{UV}$$

(b) *The matrix element of the one-electron operator*

The matrix element of h between the two determinants is obtained in a similar way to that used for the calculation of the matrix element of the identity operator:

$$\begin{aligned} \langle \Psi_U | \sum_{i=1}^N h(i) | \Psi_V \rangle &= \langle U | \sum_{i=1}^N h(i) | \sum_P (-1)^P P V \rangle \\ &= \langle U | \sum_{i=1}^N h(i) | \det(V_M) \rangle \end{aligned}$$

In the next step let us consider the first term in the one electron operator: $h(1)$. Let us introduce the notation:

$$h_{uv}(kl) = \int u_k^*(1) h(1) v_l d\tau_1$$

The ij element of the matrix V_M is equal to $v_j(i)$, i.e. all elements in row i depend on the variable i and the columns are determined by the different v_j 's. Let us expand the determinant $\det(V_M)$ according to the elements of the first row:

$$\det(V_M) = \sum_{j=1}^N (-1)^{(1+j)} v_j(1) \det[V_M(1|j)] \quad (1.24)$$

The elements $v_j(1)$ are the only ones which depend on the variable 1 , the matrix $V_M(1|j)$ is obtained from the matrix V_M by striking the row 1 and the column j . Now it is easy to calculate the matrix element of $h(1)$ and in a similar way to the one which we used for the calculation of the matrix element of the identity operator between the two determinantal functions. We obtain for the matrix element of the first term of the one electron operator the following result:

$$\begin{aligned} \langle \Psi_U | h(1) | \Psi_V \rangle &= \langle U | h(1) | \det(V_M) \rangle \\ &= \sum_{j=1}^N h_{uv}(1j) (-1)^{(1+j)} \langle u_2(2) \dots u_N(N) | \det[V_M(1|j)] \rangle \\ &= \sum_{j=1}^N (-1)^{(1+j)} h_{uv}(1j) \det[DUV(1|j)] \end{aligned}$$

The matrix $DUV(1|j)$ is obtained from the matrix D_{UV} by striking the first row and the j 'th column. In calculating the matrix elements of $h(2)$ one

expands the determinant of the matrix V_M according to the second row, and so on. The final result reads as follows:

$$\langle \Psi_U | \sum_{i=1}^N h(i) | \Psi_V \rangle = \sum_{i=1}^N \sum_{j=1}^N h_{uv}(ij) (-1)^{(i+j)} \det[D_{UV}(i|j)] \quad (1.25)$$

In Eq. (1.25) we have the determinant of matrices $D_{UV}(i|j)$ which are obtained from the matrix D_{UV} by omitting the i 'th row and the j 'th column. These are called the (i,j) *minors* of the determinant, together with the signfactors $(-1)^{(i+j)}$ they are called *cofactors*.

(c) *The matrix element of the two-electron operator.*

The first step is identical to the ones taken for the identity operator and the one-electron operator:

$$\begin{aligned} \langle \Psi_U | \sum_{i=1}^N \sum_{j>i}^N g(i,j) | \Psi_V \rangle &= \langle U | \sum_{i=1}^N \sum_{j>i}^N g(i,j) | \sum_P (-1)^P P V \rangle \\ &= \langle U | \sum_{i=1}^N \sum_{j>i}^N g(i,j) | \det(V_M) \rangle \end{aligned}$$

Let us consider the first term in the two electron operator $g(1,2)$. We shall use the Laplace expansion of the determinant $\det(V_M)$ according to the first and second rows (the elements of these rows are the only ones which depend on the variables 1 and 2.

$$\det(V_M) = \sum_{i=1}^N \sum_{j=1}^N \begin{vmatrix} v_i(1) & v_j(1) \\ v_i(2) & v_j(2) \end{vmatrix} (-1)^{(1+2+i+j)} \det[V_M(12|i,j)] \quad (1.26)$$

The matrix $V_M(12|i,j)$ is obtained from the matrix V_M by omitting the first and second rows and the k 'th and l 'th columns. We shall use the following notation:

$$\int \int u_1^*(1) u_2^*(2) g(1,2) v_k(1) v_l(2) d\tau_1 d\tau_2 = g_{uv}(12|kl)$$

Let us look first at the part of the expression which depends on the variables 1 and 2. It is easy to see that this contributes the following term:

$$\int \int u_1^*(1) u_2^*(2) g(1,2) [v_k(1) v_l(2) - v_k(2) v_l(1)] d\tau_1 d\tau_2$$

For the remaining part of the expression we can use again the same technique as used for the calculation in the previous two parts, and the result reads:

$$\begin{aligned} & \langle \Psi_U | g(1, 2) | \Psi_V \rangle \\ &= \sum_{k=1}^N \sum_{l=1}^N [g_{uv}(12|kl) - g_{uv}(12|lk)] (-1)^{(1+2+k+l)} \det[D_{UV}(12|kl)] \end{aligned}$$

The matrix $D_{UV}(12|kl)$ is obtained from the matrix D_{UV} by omitting the first and second rows and the k 'th and l 'th columns. It is quite easy to obtain the general result by using the Laplace expansions for the i 'th and j 'th rows, so we have the final result:

$$\begin{aligned} & \langle \Psi_U | \sum_{i=1}^N \sum_{j>1i}^N g(i, j) | \Psi_V \rangle \\ &= \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N \sum_{l=1}^N [g_{uv}(ij|kl) - g_{uv}(ij|lk)] (-1)^{(i+j+k+l)} \det[D_{UV}(ij|kl)] \end{aligned}$$

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2

The symmetric group

2.1 Introduction

The use of the symmetric group in quantum chemistry is the main theme of this book. This chapter summarizes the basic notions which will be used. The application of point groups is fairly well known in quantum chemistry but the symmetric group properties are less familiar. We start from the elementary notions and develop those theorems which will be used later.

2.2 Permutations

In discussing the antisymmetry principle we have defined operators which interchange different electrons. These operators are representatives of a more abstract notion: *permutation*. We shall define a permutation of N objects in which 1 is replaced by p_1 , 2 by p_2, \dots , and N by p_N . The set (p_1, \dots, p_N) consists of the numbers $(1, \dots, N)$ but arranged in a different order. The permutation will be denoted as follows:

$$P = \begin{pmatrix} 1 & 2 & \dots & N \\ p_1 & p_2 & \dots & p_N \end{pmatrix} \quad (2.1)$$

Only the vertical correspondence is essential, the columns in the above notation could be written in arbitrary order but they represent the same permutation.

The product of two permutations P and R is again a permutation. The order in which we apply the two permutations is important, as in general permutations do not commute. We first apply the permutation standing on the right and then the second permutation. This convention is different from the one used in mathematical texts, the reason for our convention is

that we apply the permutation operators to the electronic coordinates in the wavefunction which stands to the right of the operator.

$$R = \begin{pmatrix} 1 & 2 & \dots & N \\ r_1 & r_2 & \dots & r_N \end{pmatrix} \equiv \begin{pmatrix} p_1 & p_2 & \dots & p_N \\ q_1 & q_2 & \dots & q_N \end{pmatrix}$$

The product permutation is obtained as follows:

$$\begin{aligned} Q = RP &= \begin{pmatrix} p_1 & p_2 & \dots & p_N \\ q_1 & q_2 & \dots & q_N \end{pmatrix} \begin{pmatrix} 1 & 2 & \dots & N \\ p_1 & p_2 & \dots & p_N \end{pmatrix} \\ &= \begin{pmatrix} 1 & 2 & \dots & N \\ q_1 & q_2 & \dots & q_N \end{pmatrix} \end{aligned}$$

In the first permutation 1 is replaced by p_1 , in the second p_1 is replaced by q_1 , so finally 1 is replaced by q_1 . We have written the second permutation in such a form that the upper set is identical with the lower set of the first permutation. We are allowed to do this because only the vertical correspondence is important.

2.3 The symmetric group

The $N!$ permutations form a group. The product of two permutations is again a permutation, it is an element of the group. The identity element is the permutation

$$E = \begin{pmatrix} 1 & 2 & \dots & N \\ 1 & 2 & \dots & N \end{pmatrix} \quad (2.2)$$

The inverse of permutation P is the permutation:

$$P^{-1} = \begin{pmatrix} p_1 & p_2 & \dots & p_N \\ 1 & 2 & \dots & N \end{pmatrix} \quad (2.3)$$

Evidently the product of P and P^{-1} is the identity element. Finally the product of permutations is associative. As all the four postulates which characterize a group are satisfied we have a group, called the *symmetric group*. The *order* of the group i.e., the number of its elements is $N!$.

2.4 Cyclic permutation

A cyclic permutation of *length* l has the following form:

$$P = \begin{pmatrix} p_1 & p_2 & \dots & p_l \\ p_2 & p_3 & \dots & p_1 \end{pmatrix} \equiv (p_1, p_2, \dots, p_l) \quad (2.4)$$

The inverse of the cyclic permutation is obtained by reversing the order of elements in P : $P^{(-1)} = (p_l, p_{l-1}, \dots, p_1)$. Cyclic permutations of length two are called *transpositions*.

THEOREM 2.1

Every permutation can be written as a product of cyclic permutations.

We shall prove the theorem by constructing an algorithm which produces from an arbitrary permutation the product of cyclic permutations. In the original permutation 1 is replaced by $p_1 \equiv c_1$. The number c_1 is replaced by c_2, \dots , and finally c_{l-1} is replaced by 1 . If $l = N$ then we have a cyclic permutation of length N . If $l < N$ then look for a number say d_1 which does not occur among the numbers $1, c_1, \dots, c_{l-1}$ and use the same algorithm for constructing the second cycle containing the numbers d_1, \dots, d_m . If the first and second set of numbers exhaust all the numbers from 1 to N then the permutation can be written as a product of two cyclic permutations. If there are still numbers left then we continue the process until the whole permutation is obtained as a product of cyclic permutations. As the different cyclic permutations operate on different sets of numbers, they commute, so it is irrelevant in which order we write them.

THEOREM 2.2

A cyclic permutation can be written as a product of transpositions.

Let us start with a cyclic permutation of length 3.

$$C_3 = \begin{pmatrix} c_1 & c_2 & c_3 \\ c_2 & c_3 & c_1 \end{pmatrix}$$

This permutation can be written as product of two transpositions:

$$C_3 = (c_1 \ c_2)(c_2 \ c_3) = \begin{pmatrix} c_1 & c_3 & c_2 \\ c_2 & c_3 & c_1 \end{pmatrix} \begin{pmatrix} c_1 & c_2 & c_3 \\ c_1 & c_3 & c_2 \end{pmatrix} = \begin{pmatrix} c_1 & c_2 & c_3 \\ c_2 & c_3 & c_1 \end{pmatrix}$$

In a similar way we can show that a cyclic permutation of length 4 can be written as a product of three transpositions.

$$\begin{aligned} C_4 &= \begin{pmatrix} c_1 & c_2 & c_3 & c_4 \\ c_2 & c_3 & c_4 & c_1 \end{pmatrix} = \begin{pmatrix} c_1 & c_2 & c_3 \\ c_2 & c_3 & c_1 \end{pmatrix} \begin{pmatrix} c_3 & c_4 \\ c_4 & c_3 \end{pmatrix} \\ &= (c_1 \ c_2)(c_2 \ c_3)(c_3 \ c_4) \end{aligned}$$

Continuing in this way one can establish that a cyclic permutation of length l can be written as a product of $l-1$ transpositions.

$$C_l = \begin{pmatrix} c_1 & \cdot & \cdot & \cdot & c_l \\ c_2 & \cdot & \cdot & \cdot & c_1 \end{pmatrix} = (c_1 \ c_2)(c_2 \ c_3)\dots(c_{l-1} \ c_l) \quad (2.5)$$

This is not the only way one can write a cyclic permutation as a product of transpositions but we shall find the above decomposition particularly useful.

Combining theorems 2.1 and 2.2 one has the result:

THEOREM 2.3

Every permutation can be written as a product of transpositions.

The decomposition of a permutation into the product of transpositions is not unique as cyclic permutations can be decomposed in different ways into product of transpositions. But the number of transpositions in the decomposition is either even or odd and this is a unique property of a given permutation.

Parity. The parity of a permutation P is defined as $(-1)^p$, where p is the number of transpositions when we write the permutation as a product of transpositions. If this number is even the permutation is an even permutation, if it is odd we have an odd permutation. Half of the permutations are even, and the other half are odd permutations. One can see this easily in the following way: The elements E and the transposition $(1 \ 2)$ form a subgroup of S_N of order 2 (S_2). The inverse of $(1 \ 2)$ is itself and its square is the identity element. The total group can be decomposed into two cosets of S_2 . Every element of the first coset (those which are multiplied by the identity) can be written as a product of $(N-2)$ transpositions, while elements of the second coset can be expressed as products of $(N-1)$ transpositions. Hence the elements of the first coset are even permutations (if N is even) and the elements of the second are odd permutations. If N is odd then the elements of the first coset are odd permutations and the elements of the second coset are even permutations.

The product of two even permutations is again an even permutation, and the inverse of an even permutation is also an even permutation. As the identity element is an even permutation, the $N!/2$ even permutation form a group, a subgroup of S_N , it is called the *alternating group*.

THEOREM 2.4

The product $P R P^{-1}$ is a permutation obtained by operating with P on both the upper and the lower set defining the permutation R .

Let the permutation R defined as follows:

$$R = \begin{pmatrix} 1 & \cdot & \cdot & \cdot & N \\ r_1 & \cdot & \cdot & \cdot & r_N \end{pmatrix}$$